

PTO 08-0805

CC=JP DATE=20000111 KIND=A  
PN=14006330

EASILY BONDED SYNDIOTACTIC POLYSTYRENE-BASED BIAXIALLY ORIENTED FILM  
[Ekisetchakusei shinjiotakuchikku porisuchiren-kei nijiku enshin  
firumu]

Chikao Morishige, et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. November 2007

Translated by: FLS, Inc.

PUBLICATION COUNTRY (19) : JP

DOCUMENT NUMBER (11) : 2000-6330

DOCUMENT KIND (12) : A  
(13) :

PUBLICATION DATE (43) : 20000111

PUBLICATION DATE (45) :

APPLICATION NUMBER (21) : 10-177281

APPLICATION DATE (22) : 19980624

ADDITION TO (61) :

INTERNATIONAL CLASSIFICATION (51) : B32B 27/30, 7/12, 27/36

DOMESTIC CLASSIFICATION (52) :

PRIORITY COUNTRY (33) :

PRIORITY DATE (32) :

PRIORITY NUMBER (31) :

INVENTORS (72) : MORISHIGE, CHIKAO; SATO, MASAYOSHI; TANABE, MASATOSHI; MORI, KEIJI.

APPLICANT (71) : TOYOBO CO LTD

TITLE (54) : EASILY BONDED SYNDIOTACTIC POLYSTYRENE-BASED BIAXIALLY ORIENTED FILM

FOREIGN TITLE [54A] : EKISETCHAKUSEI SHINJIOTAKUCHIKU PORISUCHIREN-KEI NIJKU ENSHIN FIRUMU

[Claims]

\*

[Claim 1] An easily bonded syndiotactic polystyrene film on which an adhesion improving layer has been laminated, wherein a self-crosslinking polyester graft copolymer in which one or more type of polymerizable unsaturated monomer has been grafted to a hydrophobic polyester resin is [applied to] at least one surface of a film substantially comprising a styrene polymer with a syndiotactic structure, and wherein the graft copolymer includes at least one monomer containing an acid anhydride with a double bond.

[Claim 2] The easily bonded syndiotactic polystyrene film of claim 1, wherein a layer with the self-crosslinking polyester graft copolymer as a configurational component is formed by applying an application solution containing the self-crosslinking polyester graft copolymer to unstretched or uniaxially stretched film, drying the solution, stretching the film uniaxially or along more than one axis, and heat-fixing the film.

[Claim 3] The easily bonded syndiotactic polystyrene film of Claim 1 or Claim 2, wherein the polymerizable unsaturated monomer contains at least an anhydride of maleic acid and styrene.

[Detailed Description of the Invention]

[0001] [Technical Field of the Invention]

The present invention relates to a syndiotactic polystyrene biaxially oriented film and, more specifically to an easily bonded

---

\* Paragraph numbers correspond to the numbers in the foreign text.

syndiotactic polystyrene biaxially oriented film with superior transparency and adhesive properties.

[0002] [Prior Art]

The development of syndiotactic polystyrene biaxially oriented film with superior electrical properties and transparency has been widely anticipated with applications in the various films used in the fields of magnetic tape, photography and printing, capacitors, and packaging. If a film is used as a packaging material, a printing layer, an organic barrier layer and an inorganic or metal deposition film are usually formed on at least one side of the biaxially stretched film. Laminates on film include sealant layers with an adhesive formed using the dry laminate method and sealant layers formed using the extrusion laminate method. In bags using laminates, the opening is heat sealed after the bag has been filled with contents. Some contents packaged for general consumers include condiments such as miso or soy sauce, water-based foods such as soups and retort foods, and pharmaceutical products. When laminates are used in the prior art, an adhesion improving layer is often used to provide adhesive properties for the printing layer, organic barrier layer and sealant layer.

[0003] [Problem Solved by the Invention]

However, it is difficult to apply an adhesion improving layer to polystyrene film because of its properties. When a water-based application agent of the prior art is used, the adhesive solution is often rejected due to the low surface energy of the film, and the external appearance is poor. When an oil-based application agent is

used, the resulting impact resistance and recycling properties are poor. The purpose of the present invention is to provide a laminated syndiotactic polystyrene biaxially stretched film with superior adhesiveness to a sealant layer by using a water-based application agent that can be applied to polystyrene film and by applying this water-based application agent to film.

[0004] [Means of Solving the Problem]

In order to achieve this purpose, the present invention is an easily bonded syndiotactic polystyrene film on which an adhesion improving layer has been laminated, wherein a self-crosslinking polyester graft copolymer in which one or more type of polymerizable unsaturated monomer has been grafted to a hydrophobic polyester resin is [applied to] at least one surface of a film substantially comprising a styrene polymer with a syndiotactic structure, and wherein the graft copolymer includes at least one monomer containing an acid anhydride with a double bond.

[0005] Polystyrene polymers with a stereoregular syndiotactic structure that can be used in the present invention include polystyrene; poly(alkylstyrenes) such as poly(p-, m- or o-methylstyrene), poly(2,4-, 2,5-, 3,4- or 3,5-dimethylstyrene) and poly(p-tert-butylstyrene); poly(halogenated styrenes) such as poly(p-, m- or o-chlorostyrene), poly(p-, m- or o-bromostyrene), poly(p-, m- or o-fluorostyrene) and poly(o-methyl-p-fluorostyrene); poly(halogen-substituted alkylstyrene) such as poly (p-, m- or o-chloromethylstyrene); poly(alkoxystyrenes) such as poly(p-, m- or o-

methoxystyrene) and poly(p-, m- or o-ethoxystyrene); poly(carboxyalkylstyrenes) such as poly(p-, m- or o-carboxymethylstyrene); poly(alkyletherstyrenes) such as poly(p-vinylbenzylpropyl); poly(alkylsilylstyrenes) such as poly(p-trimethylsilylstyrene); and poly(vinylbenzyldimethoxyphosphides).

[0006] Among these polystyrene polymers, polystyrene is especially ideal for the present invention. Also, the polystyrene polymers with a syndiotactic structure used in the present invention to not have to be a single compound. If the syndiotacticity is within the proper range, they can be mixed with polystyrenes having an atactic structure or an isotactic structure. Copolymer mixtures can also be used. The polystyrene polymers used in the present invention should have a weight average molecular weight greater than 10,000, preferably greater than 50,000. If the weight average molecular weight is less than 10,000, a biaxially stretched film with superior stretching properties and heat resistance cannot be obtained. There is no particular upper limit on the weight average molecular weight, but polymers with a weight average molecular weight greater than 1,500,000 tend to break because of the higher stretching tension.

[0007] The syndiotactic polystyrene biaxially stretched film of the present invention can use any method common in the art. Examples include the successive biaxial stretching method in which vertical stretching and horizontal stretching are performed in order, or the horizontal-vertical-horizontal stretching method, the vertical-horizontal-vertical stretching method or the vertical-vertical-

horizontal stretching method. The selection can be made based on the desired strength or properties such as dimensional stability. Heat fixing, vertical relaxation and horizontal relaxation are also required. A lubricant such as inactive particles can be added to the syndiotactic polystyrene polymer. Examples of particles include metal oxides such as silica, titanium dioxide, talc and kaolinite, metal salts such as calcium carbonate, calcium phosphate and barium sulfate, and organic polymers. These can be used alone or in combinations of two or more.

[0008] (Graft Copolymer)

The graft polymerization in the present invention is usually performed by reacting a radical initiator and radical polymerizable monomer mixture in a state in which a hydrophobic copolymer polyester resin is dissolved in an organic solvent. In addition to the graft polymer between the desired hydrophobic polymer polyester and the radical polymerizable monomer mixture, the reaction product at the end of the graft reaction can include hydrophobic copolymer polyester that is not grafted or the radical polymer not grafted to the hydrophobic copolymer polyester. The graft polymer of the present invention can contain all of these.

[0009] The acid number of the reaction product in the present invention obtained from graft polymerization of the radical polymerizable monomer to the hydrophobic copolymer polyester resin should be greater than  $600 \text{ eq}/10^6$ . Ideally, the acid number of the reaction product should be greater than  $1200 \text{ eq}/10^6$ . If the acid

number of the reaction product is less than 600 eq/10<sup>6</sup>, the adhesiveness to the layer covered by the primer material is not sufficient, and this is the purpose of the present invention.

[0010] The polymerization ratio of the hydrophobic copolymer polyester resin to radical polymerizable monomer desired to achieve the purpose of the present invention should be hydrophobic copolymer polyester resin/radical polymerizable monomer = 40/60 to 95/5, preferably 55/45 to 93/7, and ideally 60/40 to 90/10. If the polymerization ratio of hydrophobic copolymer polyester resin is less than 40 wt%, the polyester resin cannot manifest superior adhesiveness. If the polymerization ratio of hydrophobic copolymer polyester resin is greater than 95 wt%, blocking tends to occur which is a shortcoming of polyester resins.

[0011] The graft polymerization reaction product of the present invention is performed in an organic solvent solution or dispersion, or a water-based solvent solution or dispersion. A water-based solvent dispersion is preferred for aqueous dispersion resins from the standpoint of the operating environment and application properties. In order to obtain an aqueous dispersion resin, a radical polymerizable monomer containing a hydrophilic radical polymerizable monomer is usually graft-polymerized to a hydrophobic copolymer polyester resin, water is added, and the organic solvent is removed. The aqueous dispersion resin in the present invention has an average particle diameter as measured using the laser beam scattering method of 500 nm or less. It is semi-transparent and has a milky white appearance. The

polymerization method can be adjusted to obtain aqueous dispersion resins with various particle diameters. The particle diameter is between 10 and 500 nm. From the standpoint of dispersion stability, however, it should be 400 nm or less and preferably 300 nm or less. If it exceeds 500 nm, the luster of the coated film surface decreases. The transparency also decreases. If less than 10 nm, the water resistance declines and good water resistance is one of the purposes of the present invention.

[0012] The hydrophilic radical polymerizable monomer used in the aqueous dispersion resin of the present invention has a hydrophilic group or has a group that can be changed into a hydrophilic group later. The radical polymerizable monomers with a hydrophilic group can be a radical polymerizable monomer with a carboxy group, hydroxyl group, phosphoric acid group, phosphorous acid group, sulfonic acid group, amide group or quaternary ammonium acid group. Groups for radical polymerizable monomers that can be changed to hydrophilic groups include acid anhydride groups, glycidyl groups and chloro groups. From the standpoint of water dispersion properties, a carboxyl group is ideal. A radical polymerizable monomer with a carboxyl group or a group becoming a carboxyl group is preferred. A radical polymerizable monomer with a carboxyl group or a group becoming a carboxyl group is also preferred from the standpoint of improving the acid number of the present invention.

[0013] (Polyester)

The hydrophobic copolymer polyester resin in the present invention should be substantially non-water soluble. In other words, it should not itself dissolve or disperse in water. When a polyester resin that disperses or dissolves in water is used in the graft polymerization, the adhesive properties and water resistance that are a purpose of the present invention are poor.

[0014] The composition of the dicarboxylic acid component in the hydrophilic copolymer polyester resin should be 60 to 99.5 mol% aromatic dicarboxylic acid, 0-40 mol% aliphaticdicarboxylic acid and/or alicyclic dicarboxylic acid, and 0.5-10 mol% dicarboxylic acid with a polymerizable unsaturated double bond. If there is less than 60 mol% aromatic dicarboxylic acid or if there is less than 40 mol% aliphatic dicarboxylic acid and/or alicyclic dicarboxylic acid, the adhesive strength declines.

[0015] If there is less than 0.5 mol% dicarboxylic acid with a polymerizable unsaturated double bond, it is difficult to efficiently graft the radical polymerizable monomer to the polyester resin. If there is more than 10 mol%, the viscosity increases in the latter stage of the grafting reaction and the reaction does not progress smoothly. Preferably, there should be 70-98 mol% aromatic dicarboxylic acid, 0-30 mol% aliphatic dicarboxylic acid and/or alicyclic dicarboxylic acid, and 2-7 mol% dicarboxylic acid with a polymerizable unsaturated double bond

[0016] Examples of aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, orthophthalic acid, naphthalene dicarboxylic acid and biphenyl dicarboxylic acid. A dicarboxylic acid with a hydrophilic group such as 5-sodium sulfoisophthalic acid is preferred from the standpoint of not reducing water resistance, which is a purpose of the present invention. Examples of aliphatic dicarboxylic acids include succinic acid, adipic acid, azaleic acid, sebacic acid, dodecanedionic acid and dimeric acid. Examples of alicyclic dicarboxylic acids include 1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid and 1,2-cyclohexane dicarboxylic acid, and their acid anhydrides.

[0017] Examples of dicarboxylic acids with a polymerizable unsaturated double bond include  $\alpha,\beta$ -unsaturated dicarboxylic acids such as fumaric acid, maleic acid, anhydrous maleic acid, itaconic acid and citraconic acid, and alicyclic dicarboxylic acids with unsaturated double bonds such as 2,5-norbornene dicarboxylic acid anhydrides and tetrahydrophthalic acid anhydrides. From the standpoint of polymerization, the most preferred are fumaric acid, maleic acid and 2,5-norbornene dicarboxylic acid.

[0018] The glycol component can be an aliphatic glycol with two to ten carbon atoms and/or an alicyclic glycol with six to twelve carbon atoms and/or a glycol with an ether bond. Aliphatic glycols with two to ten carbon atoms include ethylene glycol, 1,2-propylene glycol, 1,3-propane diole, 1,4-butane diole, 1,5-pentanediole, neopentyl glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediole, 1,9-

nonanediole, and 2-ethyl-2-butylpropanediol. Alicyclic glycols with six to twelve carbon atoms include 1,4-cyclohexane dimethanol.

[0019] Glycols with ether bonds include diethylene glycol, triethylene glycol, dipropylene glycol, and glycols obtained by adding ethylene oxide or propylene oxide to two of phenolic hydroxyl groups on a bisphenol such as 2,2-bis(4-hydroxyethoxyphenyl)propane.

Polyethylene glycol, polypropylene glycol and polytetramethylene glycol can be used if necessary.

[0020] 0-5 mol% of a trifunctional polycarboxylic acid or higher and/or polyole can be polymerized in the copolymer polyester resin used in the present invention. Examples of trifunctional polycarboxylic acids or higher include (anhydrous) trimellitic acid, (anhydrous) pyromellitic acid, (anhydrous) benzophenone tetracarboxylic acid, trimesic acid, ethylene glycol bis (anhydrotrimellitate) and glycerol tris (anhydrotrimellitate). Trifunctional polyoles or higher include glycerin, trimethylol ethane, trimethylol propane and pentaerithritol. 0-5 mol% and preferably 0-3 mol% trifunctional or higher polycarboxylic acid and/or polyole should be polymerized with all the acid components or glycol components. However, if the amount exceeds 5 mol%, gelatinization occurs during polymerization which is undesirable.

[0021] The molecular weight of the hydrophobic copolymer polyester resin should range between 5,000 and 50,000 as a weight average. If the molecular weight is less than 5,000, the adhesive

strength declines. If the molecular weight exceeds 50,000, problematic gelatinization occurs during polymerization.

[0022] (Polymerizable Unsaturated Monomer Polymer)

Examples of polymerizable unsaturated monomers of the present invention include fumaric acid and monoesters and diesters of fumaric acid such as fumaric acid monoethyl, fumaric acid diethyl and fumaric acid dibutyl; maleic acid, maleic acid anhydrides and monoesters and diesters of maleic acid such as maleic acid monoethyl, maleic acid diethyl and maleic acid dibutyl; itaconic acid, itaconic acid anhydrides and monoesters and diesters of itaconic acid; maleimides such as phenyl maleimides; styrene and styrene derivatives such as  $\alpha$ -methyl styrene, t-butyl styrene and chloromethyl styrene; vinyl toluene and divinyl benzene. Acrylic polymerizable monomers include alkyl acrylates and alkyl methacrylates (the alkyl groups including methyl groups, ethyl groups, n-propyl groups, isopropyl groups, n-butyl groups, isobutyl group, t-butyl groups, 2-ethylhexyl groups, cyclohexyl groups, phenyl groups, benzyl groups and phenylethyl groups, etc.); acrylic monomers with hydroxyl groups such as 2-hydroxymethyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate; acrylic monomers with amide groups such as acrylamide, methacrylamide, N-methyl methacrylamide, N-methyl acrylamide, N-methylol acrylamide, N-methylol methacrylamide, N,N-dimethylol acrylamide, N-methoxymethyl acrylamide, N-methoxymethyl methacrylamide and N-phenyl acrylamide; acryl monomers with amino groups such as N,N-diethylaminoethyl acrylate and N,N-

diethylaminoethyl methacrylate; acrylic monomers with epoxy groups such as glycidyl acrylate and glycidyl methacrylate; and acrylic monomers containing carboxyl groups or their salts such as acrylic acid, methacrylic acid and their salts (sodium salts, potassium salts and ammonium salts). Maleic anhydrides and their esters are preferred. These monomers can be used alone or in combinations of two or more.

[0023] The graft polymerization in the present invention is usually performed by reacting a radical initiator and radical polymerizable monomer mixture in a state in which a hydrophobic copolymer polyester resin is dissolved in an organic solvent. In addition to the graft polymer between the desired hydrophobic polymer polyester and the radical polymerizable monomer mixture, the reaction product at the end of the graft reaction can include hydrophobic copolymer polyester that is not grafted or the radical polymer not grafted to the hydrophobic copolymer polyester. The graft polymer of the present invention can contain all of these.

[0024] (Polymerization Initiators and Other Additives)

Any organic peroxide or organic azo compound common in the art can be used as the graft polymerization initiator in the present invention. Examples of organic peroxides include benzoyl peroxide and t-butyl peroxy pivalate. Organic azo compounds include 2,2'-azobis isobutyronitrile and 2,2'-azobis (2,4-dimethylvaleronitrile). The amount of polymerization initiator used to conduct graft polymerization is at least 0.2 wt% or more and preferably 0.5 wt% or more per polymerized monomer. If necessary, a chain transfer agent can

be used with the polymerization initiator to adjust the length of the branch polymer chains. Examples include octylmercaptane, mercaptoethanol and 3-t-butyl-4-hydroxyanizole. Here, it should be added in the 0-5 wt% range relative to the polymerized monomer.

[0025] (Reaction Solvent)

The graft reaction solvent used to embody the present invention should consist of a water-soluble organic solvent with a boiling point between 50 and 250°C. The solubility of the water-soluble organic solvent in 20°C water should be at least greater than 10 g/L, preferably greater than 20 g/L. If the boiling point exceeds 250°C, the evaporation rate is too slow and it cannot be removed sufficiently from the application film at high temperatures. If the boiling point is less than 50°C, it is very dangerous to use because the initiator is destroyed by the radical at temperatures under 50°C when it is used as a solvent in a graft reaction. Water-soluble organic solvents in the first group which dissolve copolymer polyester resins well and dissolve polymerizable monomer mixtures containing polymerizable monomers with carboxyl groups well include esters such as ethyl acetate; ketones such as methylethyl ketone, methylisopropyl ketone and cyclohexanone; cyclic ethers, such as tetrahydrofuran, dioxane and 1,3-dioxalane; glycol ethers, such as ethylene glycol dimethyl ether, propylene glycol methyl ether, propylene glycol propyl ether, ethylene glycol ethyl ether and ethylene glycol butyl ether; carbitols, such as methyl carbitol, ethyl carbitol and butyl carbitol; lower esters of glycals and glycol ethers, such as ethylene glycol diacetate and

ethylene glycol ethyl acetate; ketone alcohols such as diacetone alcohols; and N-substituted amides, such as dimethyl formamide, dimethyl acetoamide and N-methyl pyrrolidone.

[0026] Water-soluble organic solvents in the second group which do not dissolve copolymer polyester resins very well but dissolve polymerizable monomer mixtures containing polymerizable monomers with carboxyl groups well include water, lower alcohols, lower carboxylic acids and lower amines. In the embodiment of the present invention, alcohols with one to four carbon atoms and glycals are preferred.

[0027] If the grafting reaction is performed with a single solvent, a water-soluble organic solvent in the first group should be selected. If a mixture of solvents is used, multiple water-soluble organic solvents from the first group can be selected or one type of water-soluble organic solvent from the first group and one type of water-soluble organic solvent from the second group can be selected.

[0028] If the solvent used in the graft polymerization reaction is a single solvent selected from among the water-soluble organic solvents in the first group, or if the solvent is a mixture of water-soluble organic solvents from the first group and the second group, the graft polymerization reaction can be performed well. However, a mixture of water-soluble organic solvents from the first group and the second group are preferred from the standpoint of grafting reaction behavior, grafting reaction products and the appearance and properties of the resulting aqueous dispersion.

[0029] In the solvents of the first group, the copolymerization polyester molecular chain can become broader. In mixtures of solvents from the first group and the second groups, it can become thread-line and entwined. The viscosity of the copolymer polyester in the solution is measured and confirmed. Adjusting the solution conditions of the copolymer polyester to make intermolecular crosslinking difficult is effective at preventing gelatinization. Both highly efficient gelatinization and gelatinization prevention are achieved using a solvent mixture. The weight ratio of first group to second group solvent in the mixture should be 95/5 to 10/90, preferably 90/10 to 20/80, and ideally 85/15 to 30/70. The ideal mixing ratio is determined based on the solubility of the polyester to be used.

[0030] (Aqueous Dispersion)

The graft reaction product in the present invention should be neutralized using a basic compound. Neutralization makes it easier to disperse in water. The basic compound should be a compound that allows for film formation and which can be hardened by the addition of a hardener. Ammonia and organic amines are ideal. Preferred compounds include triethyl amine, N,N-diethyl ethanol amine, N,N-dimethyl ethanol amine, aminoethanol amine, N-methyl-N,N-diethanol amine, isopropylamine, iminobispropylamine, ethylamine, diethylamine, 3-ethoxypropylamine, 3-diethylaminopropylamine, sec-butylamine, propylamine, methylaminopropylamine, dimethylaminopropylamine, methyliminobispropylamine, 3-methoxypropylamine, monoethanolamine, diethanolamine, and triethanolamine. At least some of the basic

compound should be neutral or neutral enough to give the aqueous dispersion a pH value in the 5.0 to 9.0 range based on the amount of carboxyl groups in the grafting reaction product. If a basic compound with a boiling point below 100°C is used, there is very little residual basic compound in the film after drying. It provides superior adhesive properties to metal or inorganic deposited film, and provides superior water resistance and hot water resistant adhesive properties to the laminate.

[0031] In the aqueous dispersion produced by the present invention, the weight average molecular weight of the radical polymerizable monomer should range between 500 and 50,000. If the weight average molecular weight of the radical polymerizable monomer is less than 500, the reaction is difficult to control the grafting efficiency declines, and it is difficult to provide the copolymer polyester with a hydrophilic group. The graft polymer with the radical polymerizable monomer forms a hydrated layer with dispersed particles, and the weight average molecular weight of the graft polymer with the radical polymerizable monomer should be greater than 500 to obtain a stable dispersion with a sufficiently thick hydrated layer. The upper limit for the average weight molecular weight of the graft polymer with a radical polymerizable monomer is 50,000. Control of the molecular weight within this range is performed using a combination of monomer instillation time, polymerization time, reaction solvent, monomer composition and, if necessary, chain transfer agent and polymerization prohibitor.

[0032] In the present invention, the reaction product resulting from the graft polymerization of the radical polymerizable monomer with the hydrophobic copolymerization polyester resin has self-crosslinking properties. Crosslinking does not occur at room temperature. The heat during the drying process (1) causes a dehydration reaction of the silanol group in the reaction product and (2) causes an intermolecular reaction in the hydrogen removal reaction due to the heated radical. This causes crosslinking without using a crosslinking agent. This is the first time that the adhesive properties and water resistance that is a purpose of the present invention can be realized. The crosslinking properties of the applied film can be evaluated using different methods. However, the insolubility rate is determined using a chloroform solvent able to dissolve both the hydrophobic copolymerization polyester resin and the radical polymer. The insolubility rate of the applied film obtained by drying the film at a temperature below 80°C and performing heat treatment for five minutes at 120°C should be greater than 50% and preferably greater than 70%. If the insolubility rate of the applied film is less than 50%, the adhesive properties and the water resistance are not sufficient and blocking occurs.

[0033] The graft copolymer can be used alone to form the adhesion improving layer of the present invention or can be compounded with a crosslinking agent (hardening resin) and hardened to provide the adhesion improving layer with a high degree of water resistance.

[0034] Examples of crosslinking agents include phenol formaldehyde resins of condensates of formaldehydes such as alkylated phenols and cresols; adducts of formaldehydes and ureas, melamines and benzoguanamines; and amino resins such as alkyl ether compounds of these adducts and alcohols with one to six carbon atoms; polyfunctional epoxy compounds; polyfunctional isocyanate compounds; block isocyanate compounds; polyfunctional aziridine compounds; and oxazoline compounds.

[0035] Examples of phenol formaldehyde resins include condensates of formaldehyde and phenols such as alkylated phenols (methyl, ethyl, propyl, isopropyl or butyl), p-tert-amyl phenol, 4,4'-sec-butyldene phenol, p-tert-butyl phenol, o-, m- and p-cresol, p-cyclohexyl phenol, 4,4'-isopropylidene phenol, p-nonyl phenol, p-octyl phenol, 3-pentadecyl phenol, phenyl o-cresol, p-phenyl phenol, and xylenol.

[0036] Amino resins include methoxylated methylol urea, methoxylated methylol N,N-ethylene urea, methoxylated methylol dicyanamine, methoxylated methylol melamine, methoxylated methylol benzoguanamine, butoxylated methylol melamine, and butoxylated methylol benzoguanamine. Preferred examples include methoxylated methylol melamine, butoxylated methylol melamine, and methoxylated benzoguanamine.

[0037] Examples of polyfunctional epoxy compounds include diglycidyl ethers of bisphenol A and their oligomers, diglycidyl ethers of hydrogenated bisphenol A and their oligomers, orthophthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, terephthalic

acid diglycidyl ester, p-orthobenzoic acid diglycidyl ester, tetrahydrophthalic acid diglycidyl ester, hexahydrophthalic acid diglycidyl ester, succinic acid diglycidyl ester, adipic acid diglycidyl ester, sebacic diglycidyl ester, ethylene glycol diglycidyl ester, propylene glycol diglycidyl ester, 1,4-butanediol diglycidyl ester, 1,6-hexanediol diglycidyl ester, polyalkyleneglycol diglycidyl ester, trimellitic acid triglycidyl ether, triglycidyl isocyanate, 1,4-diglycidyloxybenzene, diglycidylpropylene urea, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, pentaerithritol triglycidyl ether, and triglycidyl ether or a glycerol alkylene oxide adduct.

[0038] These polyfunctional isocyanate compounds can be aromatic or aliphatic diisocyanates with a low molecular weight or a high molecular weight, or polyisocyanates that are trivalent or higher. Polyisocyanates include tetramethylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate, halogenated diphenylmethane diisocyanate, xylene diisocyanate, halogenated xylene diisocyanate, isophorone diisocyanate, and trimers of these isocyanate compounds. These include compounds with a terminal isocyanate group obtained by reacting an excess amount of these isocyanate compounds with a low molecular weight active hydrogen compound such as ethylene glycol, propylene glycol, trimethylol propane, glycerin, sorbitol, ethylene diamine, monoethanol amine, diethanol amine, and triethanol amine, or a high molecular weight

active hydrogen compound such as a polyester polyole, polyether polyole or polyamide.

[0039] Blocked isocyanates can be obtained by performing an addition reaction on an isocyanate compound and a blocking agent using any method common in the art. Isocyanate blocking agents include phenols such as phenol, cresol, xylanol, resorcinol, nitrophenol and chlorophenol; thiophenols such as thiophenol and methyl thiophenol; oximes such as acetoxime, methylethyl ketoxime and cyclohexanone oxime; alcohols such as methanol, ethanol, propanol and butanol; halogen-substituted alcohols such as ethylene chlorhydrin and 1,3-dichloro-2-propanol; tertiary alcohols such as t-butanol and t-pentanol; lactams such as  $\epsilon$ -caprolactam,  $\delta$ -valerolactam,  $\nu$ -butyrolactam and  $\beta$ -propyllactam; aromatic amines; active methylene compounds such as acetyl acetone, acetoacetic acid ester, and malonic acid ethyl ester; mercaptans; imines; ureas; dialyl compounds; and calcium bisulfite soda.

[0040] These crosslinking agents can be used alone or in combinations of two or more. The amount of crosslinking agent used should range between 5 ppw and 40 ppw per 100 ppw grafted copolymer. Crosslinking agent compounding methods include (1) directly dissolving or dispersing a water-based crosslinking agent in an aqueous solvent solution or dispersant of the grafted copolymer, and (2) adding an oil-based crosslinking agent to the reaction solution after the grafting reaction has been completed. The method used depends on the

type and properties of crosslinking agent used. A hardening agent or accelerating agent can be combined with the crosslinking agent.

[0041] The graft copolymer can be used alone to form the adhesion improving layer of the present invention or the adhesion improving layer can include various additional resins for other purposes. These include general polyester resins, urethane resins, acrylic resins and their copolymers; various water-based resins and functional resins; conductive resins such as polyanilines and polypyrroles; UV absorbing resins; and gas barrier resins.

[0042] The adhesion improving layer can contain additives such as surfactants, antistatics, inorganic lubricants, organic lubricants and UV absorbents as long as the amounts added do not compromise the effect of the present invention.

#### [0043] [Working Examples]

The following is an explanation of the present invention with reference to working examples. In this working examples, all parts refer to parts per weight, and all percentages to weight percentages. The measurements used the following methods.

##### (1) Film Haze

The surface haze was determined using integrating sphere-type HTR Meter SEP-H2D manufactured by Japan Precision Optics Co. Ltd. in accordance with JIS-K6714.

##### (2) Adhesiveness Evaluation

A laminate was peeled in water at 90 degrees using the Tensilon UTM2 manufactured by Toyo Measuring Devices Co. Ltd., and the S-S

curve between the adhesion improving layer and the substrate layer was measured.

[0044] Working Example 1

75 parts copolymer polyester resin (A-1), 56 parts methylethyl ketone and 19 parts isopropyl alcohol were added to a reaction vessel with a stirrer, thermometer, reflux device and fixed quantity instilment device. The contents were heated and stirred at 65°C to melt the resin. After the resin had completely melted, 15 parts maleic anhydride was added to the polyester solution. Next, a solution consisting of 10 parts styrene and 1.5 parts azobis dimethyl valeronitrile dissolved in 12 parts methylethyl ketone was instilled in the polyester solution at a rate of 0.1 ml/min. This was stirred continuously for two hours. After performing analysis sampling using the reaction solution, 5 parts methanol was added. Next, 300 parts water and 15 parts triethyl amine were added to the reaction solution, and this was stirred for one hour. Afterwards, the temperature of the reaction vessel was increased to 100°C, and the methylethyl ketone, isopropyl alcohol, and excess triethyl amine were removed via distillation to obtain aqueous dispersion graft resin (B-1). Aqueous dispersion graft resin (B-1) was pale yellow and transparent.

[0045] This aqueous dispersion graft resin (B-1) was diluted in water : isopropyl alcohol = 9:1 (weight ratio) to a solid component concentration of 10%, and the application solution was adjusted. Polymer chips consisting of 3.0 wt% crosslinked polystyrene particles added to 100 wt% syndiotactic polystyrene (weight average molecular

weight: 300,000) as a lubricant, polymer chips consisting of 2.0 wt% crosslinked polystyrene particles added to 100 wt% syndiotactic polystyrene (weight average molecular weight: 300,000) as a lubricant, and polymer chips without any lubricant were mixed together at a 1:1:8 mixing ratio (weight ratio), dried, melted at 295°C, extruded from a 200 μm T type lip cap, and adhered, cooled and solidified using 40°C cooling rollers and the electrostatic charge method to obtain a 55 μm amorphous sheet.

[0046] This amorphous sheet was pre-heated to 98°C using rollers, heated using four infrared heaters with a surface temperature of 750°C, stretched by a factor of 3.3 vertically at a film temperature of 140°C, stretched by a factor of 1.2 vertically using 120°C rollers, and relaxed vertically 12% between a 150°C ceramic roller and a 40°C metal roller. Next, the application solution was applied using the die coater method, and dried using 70°C forced hot air. Using tenters, the film was pre-heated to 110°C, stretched horizontally by a factor of 3.5 at stretching temperature of 120°C, and heat-fixed for 10 seconds at 265°C. Afterwards, 5% horizontal relaxation was performed at 230°C, and 3% vertical relaxation was performed between a 220°C ceramic roller and a 40°C metal roller. In this way, a biaxially stretched syndiotactic polystyrene film was obtained with a film thickness of 4 μm. The final amount of coating agent applied was 0.1 g/m<sup>2</sup>. The results of an evaluation of this syndiotactic polystyrene film are shown in Table 2.

[0047] Working Example 2

An aqueous dispersion graft resin (B-2) was obtained in the same manner as the first working example except that the components were changed to 8 parts maleic anhydride and 17 parts styrene. Aqueous dispersion graft resin (B-2) was pale yellow and transparent. A laminated syndiotactic polystyrene film was obtained in the same manner as the first working example using aqueous dispersion graft resin (B-2). The evaluation results for this syndiotactic polystyrene film are shown in Table 2.

[0048] Working Example 3

An aqueous dispersion graft resin (B-4) was obtained in the same manner as the first working example using copolymer polyester resin (A-2) instead of (A-1). Aqueous dispersion graft resin (B-4) was pale yellow and transparent. A laminated syndiotactic polystyrene film was obtained in the same manner as the first working example using aqueous dispersion graft resin (B-2) [sic]. The evaluation results for this syndiotactic polystyrene film are shown in Table 2.

[0049] Comparative Example 1

A syndiotactic polystyrene film was obtained in the same manner as the first working example except without an adhesion improving layer. The evaluation results are shown in Table 2.

[0050] Comparative Example 2

75 parts copolymer polyester resin (A-1), 56 parts methylethyl ketone and 19 parts isopropyl alcohol were added to a reaction vessel with a stirrer, thermometer, reflux device and fixed quantity

instilment device. The contents were heated and stirred at 65°C to melt the resin. After the resin had completely melted, a solution consisting of a mixture of 17.5 parts methacrylic acid and 7.5 parts ester acrylate as well as 1.2 parts azobis dimethyl valeronitrile dissolved in 25 parts methylethyl ketone was instilled in the polyester solution at a rate of 0.2 ml/min. This was stirred continuously for two hours. After performing analysis sampling using the reaction solution, 300 parts water and 25 parts triethyl amine were added to the reaction solution, and this was stirred for one hour. Afterwards, the temperature of the reaction vessel was increased to 100°C, and the methylethyl ketone, isopropyl alcohol, and excess triethyl amine were removed via distillation to obtain aqueous dispersion graft resin (B-5). Aqueous dispersion graft resin (B-5) was pale yellow and transparent. A laminated syndiotactic polystyrene film was obtained in the same manner as the first working example using this aqueous dispersion graft resin. The evaluation results for this syndiotactic polystyrene film are shown in Table 2.

[0051] [Effect of the Invention]

As described above, the present invention with the configuration described in the claims of this patent can be used to provide a laminated syndiotactic polystyrene biaxially stretched film with superior transparency and adhesive properties.

[0052] [Table 1]

Copolymer Composition (mol%)	A-1
Terephthalic Acid	70
Sebacic Acid	26
Fumaric Acid	4
Ethylene Glycol	50
1,4-Butanediol	50
Weight Average Molecular Weight	20000

[0053] [Table 2]

	Haze (%)	Adhesive Strength (g/15 mm)	Overall Evaluation
Working Example 1	4.5	180	◎
Working Example 2	4.6	170	◎
Working Example 3	4.5	150	○
Comparative Example 1	4.1	20	□
Comparative Example 2	6.2	50	✗